

Low temperature transport properties of multigraphene structures on 6H-SiC obtained by thermal graphitization: evidences of a presence of nearly perfect graphene layer.

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Abstract.

Transport properties of multigraphene layers on 6H-SiC substrates fabricated by thermal graphitization of SiC were studied. The principal result is that these structures were shown to contain a nearly perfect graphene layer situated between the SiC substrate and multigraphene layer. It was found that the curves of magnetoresistance and Shubnikov-de Haas oscillations shown the features, typical for single-layered graphene. The low temperature resistance demonstrated an increase with temperature increase, which also corresponds to a behavior typical for single-layered graphene (antilocalization). However at higher temperatures the resistance decreased with an increase of temperature, which corresponds to a weak localization. We believe that the observed behavior can be explained by a parallel combination of contributions to the conductivity of single-layered graphene and of multigraphene, the latter allowing to escape damages of the graphene by atmosphere effect.

1. Introduction

At last time one of the popular methods of graphene layers formation is thermal graphitization of monocrystalline silicon carbide at vacuum or in argon atmosphere [1]. This method gives a possibility - in contrast to standard approaches - to fabricate large graphene samples, allowing the following lithography treatment. The essence of this method is non-stoichiometric vaporizing of silicon from a surface of mono-crystalline SiC at high temperature heating leading to a formation of hexagonal lattice of the rest carbon atoms at its surface. A quality of the layers obtained is controlled by methods of pre-grow treatment of the SiC substrate. Note that, as we know, this method most probably leads to a formation of multilayered structure. Thus we believe that the study of such structures is an important problem for the graphene physics and technology.

In our previous paper [2] we studied structure and transport properties of multigraphene layers, subjected to pre-grow thermal treatment. The obtained

multigraphene layers had properties of 2D hole gas with relatively high carrier concentration (10^{12}cm^{-2}) and low mobility $100 \text{ cm}^2/(\text{Vs})$. Temperature curves of resistance and magnetoresistance (including low field negative magnetoresistance peak) demonstrated weak localization effects. However we have not observed specific transport properties related to a nature of carriers in single-layered graphene and to a specific density of states spectrum [3], like weak antilocalization (WAL) and Shubnikov-de Haas oscillations.

In this paper we studied transport properties of more perfect graphene layers on SiC substrate, grown by sublimation in vacuum. In this case the transport properties of the obtained samples clearly demonstrated the features, typical for graphene layers. In particular, it was shown, that the behavior observed can be explained only as a result of combination of parallel contributions to conductivity of single-layered graphene and of multigraphene. This conclusion seems to be of principal importance since the structure under study is shown to contain nearly perfect graphene layer isolated from atmosphere by the multigraphene. The latter has much less conductivity with respect to the graphene layer and thus does not affect significantly the properties of the graphene.

2. Experiment

For studies of the transport properties of graphene films we used samples obtained on the surface of monocrystalline silicon carbide by sublimation in vacuum [4]. As the substrate we used semiinsulating plates 6H-SiC fabricated by CREE Inc. The graphene film was grown on the face $C_{(000\bar{1})}$. Directly before a growth of the graphene film the standard procedure of the washing of substrates in organic solvents was applied. To remove the surface layer disturbed by polishing of the plates we applied a technology of pre-growth treatment of SiC substrates developed earlier [5]. This technology allows to improve significantly a quality of the grown graphene with respect to the growth on an untreated substrate. A growth of graphene films was carried out in high-vacuum chamber with a residual pressure 10^{-6} atm.. The growth temperature was 1400-1500 C, the growth time was 15-30 min. A quality of the grown films was controlled "ex-situ" with a help of atomic-force microscopy (AFM) and of Raman spectroscopy. After the growth structures of the Hall bar geometry were formed on the graphene film (a distance between the probes $L = 20 \mu\text{m}$, a width of the graphene strip was $W = 10 \mu\text{m}$).

This structure was investigated with a help of a transparent high-resolution electron microscopy. The sample for investigation was prepared according to a standard method including a mechanic polishing of the transversal cut with a following ion etching. The investigations were made with a help of a transparent electron microscope. As a result, a typical image of a transversal cut of the structure graphene-SiC was obtained (see Fig.1).

The first graphene layer (layer 0) was situated directly on the surface of silicon carbide. Note that the distance between the last layer of the silicon carbide and the first graphene layer was only 2Å. This fact evidences a presence of a covalent binding between

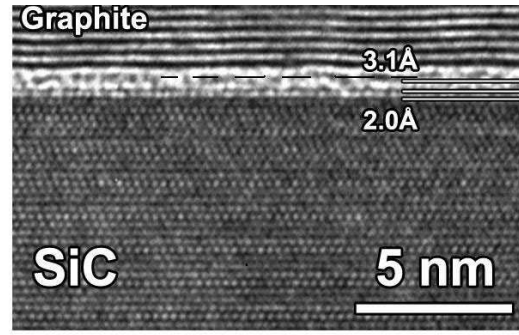


Figure 1. ??.

The image of a transversal cut of the structure graphene/SiC, obtained with a help of a high resolution transparent electron microscopy. A dotted line represents the graphene layer. 1.

Si atoms of the last layer of SiC and C atoms of the first graphene layer. As it was shown in [6], the first layer has a function of the buffer layer and has a semiconducting character (giving a small contribution to conductivity at low temperatures). The next graphene layer (layer 1) is situated at a distance about 3.1 Å from the layer 0. The next layers (including 8 layers) are situated at distances 3,39 Å from each other. This value is close to the value of the interlayer distance in graphite and is characteristic for the Van der Waalse bondings. Thus, the electron-microscopic studies imply a presence of 3-layered structure: layer 0 - the buffer layer, not participating in the conductance, layer 1 - the layer of "perfect" graphene and the multigraphene layer (including 8 layers).

The galvanomagnetic effects studies were made on the sample with standard Hall geometry and included three orientations of the sample with respect to the magnetic field \mathbf{B} ($\mathbf{n} \parallel \mathbf{B} \perp \mathbf{j}$, $\mathbf{n} \perp \mathbf{B} \perp \mathbf{j}$, $\mathbf{n} \perp \mathbf{B} \parallel \mathbf{j}$), where \mathbf{n} and \mathbf{j} are the vectors of the normals with respect to the layers planes and to the current density, respectively. At magnetic fields 0-15 T we measured the Hall effect and magnetoresistance. According to the sign of the Hall effect we had specified the hole type of the conductivity at the whole region of temperatures (1,5 - 130 K). The Hall hole concentration, extracted at weak magnetic fields (up to $B = 1$ T) appeared to be equal to $= 8,3 \cdot 10^{12} \text{cm}^{-2}$ while at high magnetic fields (B up to 15 T) $= 1,1 \cdot 10^{13} \text{cm}^{-2}$ at $T=4,2$ K. The calculated value of the Hall mobility appeared to be $77 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at $T = 1.5$ K, which is much smaller than in single-layered epitaxial graphene ($5000\text{-}10000 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) [3].

The general pattern of the magnetoresistance (MR) curves at the fields up to 5 T is present on Fig.1

It is seen, that at high fields ($B > 1$ T) at low temperatures ($T < 15$ K), a non-monotonous contribution to the signal had appeared. The corresponding oscillations were periodic on the scale of the inverse fields (SdH oscillations). In the case of the sample plane orientations parallel to the the axis of the magnetic field ($\mathbf{n} \perp \mathbf{B} \perp \mathbf{j}$, $\mathbf{n} \perp \mathbf{B} \parallel \mathbf{j}$) the SdH oscillations were absent which evidences the 2D character of conductivity of the studied samples.

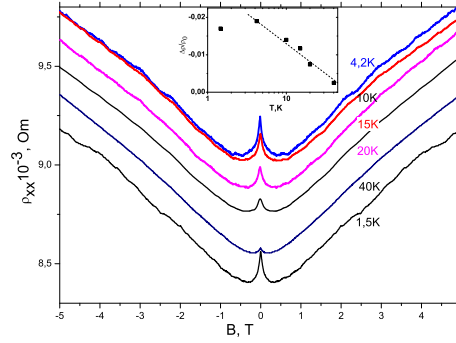


Figure 2. 2.

The curves of magnetoresistance at different temperatures. At the insert - the temperature dependence of the negative MR peak.

At the region of weak magnetic fields ($B < 0.5$ T) the effect of negative magnetoresistance (NMR) was found, Fig. 1. The temperature behavior of the NMR peak (insert in Fig.1) appeared to be proportional to $\ln T$, and thus it can be ascribed to the weak localization effect (WL) for the diffusive transport of 2D carriers. Such an interpretation of this peak is supported by the following facts:

- 1) An absence of the WL effect for the magnetic field directions parallel to the plane of the sample,
- 2) A decrease of the WL effect with an increase of temperature proportionally to $\ln T$ up to its complete suppression at $T > 50$ K.

With a decrease of temperature up to 1.5 K an increase of the WL peak is replaced by its suppression. At magnetic fields higher than 0.3 T the crossover to the positive magnetoresistance (PMR) is observed. The observed crossover with an increase of the magnetic field can be related to a manifestation of the anti-localization addition to the classical Drude conductivity. Such a behavior is similar to the magnetoresistance related to the weak antilocalization, observed in [3] for epitaxial single-layered graphene, grown on 4H-SiC.

The temperature dependence of resistance, Fig. 3, at the region 10- 100 K is also described by the logarithmic law, typical for WL (the curves slope gives for the prelogarithmic factor a resistance value about 3 kOhm (which is close enough to \hbar/e^2). At Fig. 2 it is seen, that at $T < 7$ K a reversal of the sign of the slope of temperature behavior (to the metallic behavior) is observed. This could be related to the manifestation of the WAL in systems with spin-orbital coupling [7]. However, according to the theoretical considerations concerning the nature of carriers in single-layered graphene and its specific density of state spectrum [3], in graphene WAL has not the spin-orbital character, but is rather controlled by the intervalley scattering. Experimentally, WAL had been observed in single layered graphene magnetoresistance at stronger magnetic fields, than WL [8]. In our sample the MR curves (Fig.1) also demonstrate a transition to the PMR at the fields $0.2T > B > 0.5T$, which can be

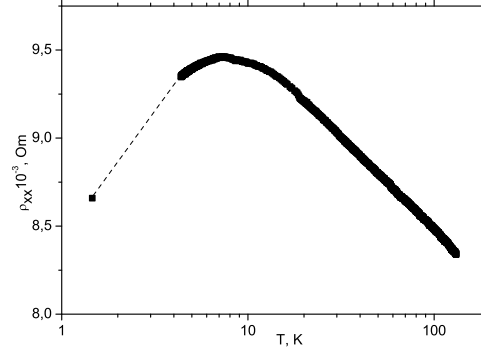


Figure 3. 3 The temperature dependence of resistance .

also related to a manifestation of WAL. However, as we know, until now a transition to the metallic behavior of conductivity in single-layered graphene at low temperatures and $B = 0$ was not observed. An exclusion is the paper, where such a quasimetallic behavior was observed at thick enough multigraphene layers (20 nm) and was ascribed to a contribution of the interfaces [9].

At high fields the SdH oscillations were observed

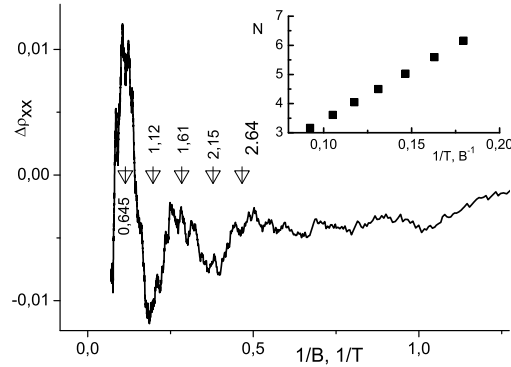


Figure 4. 4.

A curve of magnetoresistance in the scale of inverse magnetic fields, obtained by a subtraction of the background MR (described by a polynomial of a second order). The insert gives the Landau numbers as a function of the positions of SdH maxima, corresponding to the oscillations of the second type, observed at high magnetic fields).

The Fig. 3 presents a resistance behavior as a function of magnetic field, obtained by a subtraction from the MR curve of the polynomial of the second order. It is seen, that in terms of the inverse magnetic fields the pronounced oscillations with a period $\Delta = 0,17621/T$ are observed. The value of the carrier concentration, extracted from the period of the low-temperature SdH oscillations with an account of spin and value splitting for the parabolic spectrum gives $p = 2e/\Delta\hbar\pi = 2,7 \cdot 10^{11} \text{cm}^{-2}$. In addition to these oscillations, the Fig.3 also demonstrates weaker structure, which is pronounced

only up to temperatures 30 K. When separating these oscillations, one also find that these are periodic in terms of the inverse magnetic field, and its period is $\Delta = 0,0291/T$ (see insert in Fig. 3). This corresponds to the carrier concentration $p = 1,7 \cdot 10^{12} \text{cm}^{-2}$ which is by an order of magnitude higher than the concentration mentioned above. While these oscillations are observed at higher magnetic fields, one can expect that they are controlled by a layer with a lower conductivity (multigraphene).

3. Discussion

The experimental results presented above evidence, on the one hand, that the system under study manifests properties, typical for "dirty" metal (weak localization and relatively small mobilities). On the other hand, we observed weak antilocalization and SdH oscillations, which is typical for clean single-layered graphene. These facts allows to suggest, that in the system, in addition to the layer of perfect graphene, also exists a layer of multigraphene with large number of defects. We believe that the most unexpected feature is the "reversed" temperature dependence of resistance with respect to the one common for graphene. As it is known, in the first approximation the temperature dependent contribution to the graphene resistance has a form

$$2(1/\pi h) \ln(\tau_\varphi/\tau_{tr}) \quad (1)$$

where $\tau_\varphi(T)$ is the phase breaking time, τ_{tr} is the transport relaxation time in graphene while factor 2 is related to independent contributions of the two valleys. Here it is assumed that $\tau_\varphi < \tau_{iv1}$, where τ_{iv1} is the intervalley scattering time in the graphene layer which is expected to be large enough. Indeed, this time is related to the acts of scattering involving large change of the wave vector (of the order of the vector of the reciprocal lattice). Correspondingly, it is expected that at reasonable temperatures the contribution in question increases with a decrease of temperature (antilocalization). Note however that the temperature dependence of τ_{tr} can lead to violation of this conclusion. Namely, while during the temperature decrease one expects a saturation of τ_{tr} , the ratio τ_φ/τ_{tr} can, in principle, decay with the temperature increase, which leads to non-monotonous temperature behavior of the logarithm argument. However, this factor still does not allow to explain other features of the system in question. Thus let us assume, that in addition to the layer of "perfect" graphene our system also contains a conductive layer with small values of τ_{iv} - in particular, formed from multilayer material with different position of the cells and with klarge number of interlayer defects. In this case at high enough temperatures the situation $\tau_{iv,2} < \tau_{\varphi,2}$ can be realized. Here we denoted parameters corresponding to the second layer by index 2 while in the following we denote the parameters of the graphene layer by index 1. The contribution of this second layer to conductivity is controlled by the weak localization, since there is a strong mixing between the valleys, and the corresponding contribution can be described as

$$-(1/\pi h) \ln(\tau_{\varphi 2}/\tau_{tr,2}) \quad (2)$$

Thus we simultaneously have two contributions, which can manifest itself at different temperatures: the contribution of weak localization, related to the defect layer, and the contribution of antilocalization, related to more perfect graphene layer. Having in mind a summation of the two contributions, we obtain for the interference addition

$$(1/\pi h) \ln ((\tau_{\varphi 1}/\tau_{tr1})^2(\tau_{tr2}/\tau_{\varphi 2})) \quad (3)$$

As it is seen, at low temperatures the dominant contribution of the antilocalization is expected, while at higher temperatures - the dominant contribution of the weak localization. To estimate the temperature behavior of conductivity, let us consider the situation in more detail, calculating the temperature derivative of the interference addition:

$$2 \frac{\tau_{tr1}}{\tau_{\varphi 1}} \frac{\partial(\tau_{\varphi 1}/\tau_{tr1})}{\partial T} - \frac{\tau_{tr2}}{\tau_{\varphi 2}} \frac{\partial(\tau_{\varphi 2}/\tau_{tr2})}{\partial T} \quad (4)$$

According to the model suggested ("pure" graphene layer shunted by "dirty" multigraphene layer) one can make the following assumptions. First, one expects that $\tau_{tr1} > \tau_{tr2}$. Secondly, the behavior of $\tau_{\varphi 2}$ is typical for disordered materials and exhibits a saturation with temperature decrease (see, e.g., [10],[11]). Thus one can expect that at low temperatures the temperature derivative is controlled by the first term (antilocalization related to the graphene layer) while the second term is suppressed by the weak dependence of $\tau_{\varphi 2}(T)$. However with temperature increase the dominant role is played by the second term (weak localization related to the multigraphene layer). Such a behavior is emphasized by the relative small value of τ_{tr2} . It is clear that the conductivity minimum (and thus resistivity maximum) is reached when the expression of 4 vanishes. One can also expect, that the approximate estimate of the minimum temperature corresponds to approximate equality between the contributions of the localization and of the antilocalization.

Note that the further decrease of temperature, leading to violation of the inequality $\tau_{\varphi 1} < \tau_{iv1}$ can lead to an increase of resistance with temperature decrease, that is to restoration of the weak localization.

As for magnetoresistance, it is natural to expect, that at high temperatures the contribution of weak localization is emphasized, while at lower temperatures this contribution decreases. It is this behavior which is demonstrated by temperature behavior of magnetoresistance, where the low field peak of negative magnetoresistance is suppressed with temperature decrease.

As for the observation of Shubnikov - de Haas oscillations, it does not contradict to the model suggested. Namely, it is the highly conducting graphene layer with carrier concentration $p = 2,7 \cdot 10^{11} cm^{-2}$ which is responsible for these oscillation, although their amplitude is partly suppressed by a presence of the layer with low conductivity. At the same time, the carrier concentration extracted from the Hall effect $p = 8,3 \cdot 10^{12} cm^{-2}$ is formed mostly by the multigraphene layer.

Concluding, it is instructive to emphasize a role of the multigraphene layer. On the one hand, it makes a picture of the conductivity for the structure graphene/SiC to be

more complex. But, on the other hand, the multigraphene play a protecting role for the graphene layer, preventing its contact with the atmosphere. As it is known, the effect of atmosphere, leading, in particular, to a formation of background dopants, gives a significant limitation to application of single-layered graphene. Then, the multigraphene provides a good adhesion of the metal to the graphene layer in course of fabrication of contacts. The principal result of our studies is that for structures, produced by thermal graphitization of SiC still contain nearly perfect graphene layer in between of SiC substrate and multigraphene layer. Thus, the corresponding multilayered graphene structure can have advantages with respect to single-layered graphene.

4. Acknowledgements

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